

IN THE CLAIMS

1-59 (canceled)

30. (withdrawn) A fluorine-modified one- or two-component polyurethane resin, prepared by the process of

- a) preparing a fluorine-modified polyurethane prepolymer having free isocyanate groups or free amino and/or hydroxyl groups, or a fluorine-modified polyol mixture having free hydroxyl groups (binder), by
 - a₁) a fluorine-modified macromonomer (A1) having two or more amino and/or hydroxyl groups that are reactive toward isocyanate groups and having a molecular mass of 500 to 2000 daltons, a higher molecular mass polyol component (A2) having two or more hydroxyl groups that are reactive toward isocyanate groups and having a molecular mass of 500 to 6000 daltons, and, optionally, a low molecular mass polyol component (A3)(i) having two or more hydroxyl groups that are reactive toward isocyanate groups and having a molecular mass of 50 to 499 daltons

either

is reacted with a polyisocyanate component (B)(i), consisting of at least one diisocyanate, polyisocyanate, polyisocyanate derivative or polyisocyanate homolog having two or more (cyclo)aliphatic or aromatic isocyanate groups of same or different reactivity, optionally in the presence of a solvent component (L)(i) and optionally in the presence of a catalyst,

or

is blended in the presence of a solvent component (L)(i) and optionally in the presence of a catalyst,

a₂) the fluorine-modified polyurethane prepolymer or polyol mixture from stage a₁) is optionally reacted with an unmodified or fluorine-modified functionalizing component (C)(i) having one or more amino and/or hydroxyl groups that are reactive toward isocyanate groups and/or one or more isocyanate groups that are reactive toward hydroxyl groups and having a molecular mass of 50 to 2500 daltons, selected from the groups of the (cyclo)aliphatic and/or aromatic polyols and/or polyamines and/or polyamino alcohols and/or reactive polyhedral oligomeric polysilsesquioxanes (POSS) of the general formula (RSiO_{1.5})_n with n = 4, 6, 8, 10, 12 and R = any organic residue having 1 to 100 C atoms and 0 to 50 N and/or 0 to 50 O and/or 0 to 50 F and/or 0 to 50 Si and/or 0 to 50 S atoms and a molar mass of 250 to 25 000 daltons,

a₃) the fluorine-modified polyurethane prepolymer or polyol mixture from stages a₁) or a₂) is admixed with a formulating component (F)(i),

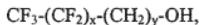
and finally

b) by preparing a fluorine-modified polyurethane resin having a polymer-bonded fluorine content of 1% to 4% by weight in the system as a whole by reacting the fluorine-modified polyurethane prepolymer from stage a₃) in the case of a one-component application with atmospheric moisture, or reacting the fluorine-modified polyurethane prepolymer or polyol mixture from stage a₃) (binder) in the case of a two-component application with a crosslinker component (D) (curing agent), with a formulating component (F)(ii) optionally in the presence of a solvent component (L)(iii) and also of a catalyst, using as crosslinker component (D) in the case of the polyol mixture from stage a₃) a polyisocyanate component (B)(iii) consisting of at least one diisocyanate, polyisocyanate, polyisocyanate derivative or polyisocyanate homolog having two or more (cyclo)aliphatic or aromatic isocyanate groups of same

or different reactivity and in the case of the polyurethane prepolymer a polyisocyanate component (B)(iii) or a low molecular mass polyol component (A3)(ii) having two or more hydroxyl groups that are reactive toward isocyanate groups and having a molecular mass of 50 to 499 daltons and/or a low molecular mass polyamine component (E) having two or more (cyclo)aliphatic or aromatic amino groups that are reactive toward isocyanate groups and having a molecular mass of 50 to 500 daltons.

31. (withdrawn) The fluorine-modified polyurethane resin of claim 30, wherein the fluorine-modified macromonomer (A1) has been prepared by

c₁) reacting a fluoro alcohol component (A4) consisting of a perfluoroalkyl alcohol having terminal methylene groups (hydrocarbon spacers), of the general formula



with x = 3 - 20 and y = 1 - 6

or of a hexafluoropropene oxide (HFPO) oligomer alcohol of the general formula



with z = 1 - 10

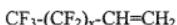
or else mixtures of these having a hydroxyl group that is reactive toward isocyanate groups and having a molecular mass of 250 to 5000 daltons, with a polyisocyanate component (B)(ii) consisting of at least one diisocyanate, polyisocyanate, polyisocyanate derivative or polyisocyanate homolog having two or more (cyclo)aliphatic or aromatic isocyanate groups of same or different reactivity, optionally in the presence of a solvent component (L)(ii) and optionally in the presence of a catalyst,

c₂) optionally reacting the preadduct from stage c₁) completely with a functionalizing component (C)(ii) having two or more amino and/or hydroxyl groups that are reactive toward isocyanate groups and having a molecular mass of 50 to 500 daltons, selected from the group of (cyclo)aliphatic and/or aromatic polyols and/or polyamines and/or polyamino alcohols.

32. (withdrawn) The fluorine-modified polyurethane resin of claim 30, wherein the fluorine-modified macromonomer (A1) is a reaction product or macromonomer, with a monomodal molar mass distribution, of monofunctional perfluoroalkyl alcohols, isophorone diisocyanate or toluene diisocyanate, and diethanolamine.

33. (withdrawn) The fluorine-modified polyurethane resin of claim 30, wherein as fluorine-modified macromonomer (A1) is an optionally solvent-containing reaction product of

i) perfluoroalkylalkenes and diethanolamine, preferably perfluoroalkylalkenes having terminal methylene groups (hydrocarbon spacers), of the general formula



with x = 3 – 20

and/or

ii) alkyl (per)fluoro(meth)acrylates and/or (per)fluoroalkyl (meth)acrylates and/or (per)fluoroalkyl (per)fluoro(meth)acrylates and diethanolamine

or

(per)fluoroalkylalkylene oxides and N-methylethanolamine or diethanolamine with preferred (per)fluoroalkylalkylene oxides of the general formula



with $x = 3 - 20$.

34. (withdrawn) The fluorine-modified polyurethane resin of claim 30, wherein the higher molecular mass polyol component (A2) is a (hydrophobically modified) polyalkylene glycol, an aliphatic or aromatic polyester, a polycaprolactone, a polycarbonate, a hydroxy-functional macromonomer or a telechelic such as α,ω -polymethacrylatediols, α,ω -dihydroxyalkylpolydimethylsiloxanes, hydroxy-functional epoxy resins, hydroxy-functional ketone resins, hydroxy-functional polysulfides, hydroxy-functional triglycerides, oxidatively drying alkyd resins based on bisepoxides and unsaturated fatty acids, or mixtures thereof.

35. (withdrawn) The fluorine-modified polyurethane resin of claim 30, wherein component (A2) is a linear or difunctional (hydrophobically modified) polyether- or polyester- or polycaprolactone- or polycarbonate-polyol or an α,ω -polymethacrylatediol having a molecular mass of 500 to 3,000 daltons.

36. (withdrawn) The fluorine-modified polyurethane resin of claim 30, wherein component (A3)(i) and (A3)(ii) is at least one of 1,4-butanediol or 2-methyl-1,3-propanediol or 2,2-dimethyl-1,3-propanediol.

37. (withdrawn) The fluorine-modified polyurethane resin of claim 30, wherein components (B)(i) and/or (B)(ii) and/or (B)(iii) are selected from difunctional polyisocyanate derivatives and/or reaction products of at least trifunctional aliphatic or aromatic polyisocyanates and optionally fluorine-modified amino-functional polyhedral oligomeric polysilsesquioxanes (POSS) of the general formula $(\text{RSiO}_{1.5})_n$ with $n = 4, 6, 8, 10, 12$ and R = any organic residue having 1 to 100 C atoms and 0 to 50 N and/or 0 to 50 O and/or 0 to 50 F and/or 0 to 50 Si and/or 0 to 50 S atoms.

38. (withdrawn) The fluorine-modified polyurethane resin of claim 30, wherein component (C)(i) comprises reactive polyhedral oligomeric polysilsesquioxanes (POSS) of the general formula $(RSiO_{1.5})_8$ with R = aminopropyl and/or isocyanatopropyl and optionally $CH_2CH_2CF_2CF_2CF_2CF_2CF_2CF_3$ and/or H and/or C_1-C_{25} -alkyl and/or C_3-C_{25} -cycloalkyl and/or C_6-C_{30} -aryl and/or $(CH_2)_3(OCH_2CH_2)_nOMe$ and/or epoxypropyl and/or dimethoxysilyloxy and/or methacryloyloxypropyl and/or triethoxysilylpropyl.

39. (withdrawn) The fluorine-modified polyurethane resin of claim 30, wherein component (C)(i) is a reactive polyhedral oligomeric polysilsesquioxanes (POSS) of the general formula



with a = 0 or 1

b = 0 or 1

a+b = 1

m = 4, 6, 8, 10, 12,

and

R is a hydrogen atom, alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl or cycloalkynyl group or polymer unit, which in each case is substituted or unsubstituted, or further functionalized polyhedral oligomeric silicon-oxygen cluster units, which are attached via a polymer unit or a bridging unit,

X is oxy, hydroxy, alkoxy, carboxy, silyl, alkylsilyl, alkoxyisilyl, siloxy, alkylsiloxy, alkoxyisiloxy, silylalkyl, alkoxyisilylalkyl, alkylsilylalkyl, halogen, epoxy, ester, fluoroalkyl, isocyanate, blocked isocyanate, acrylate, methacrylate, nitrile,

amino, phosphine or polyether group or substituents of type R that contain at least one such group of type X,

the substituents of type R and the substituents of type X each being identical or different.

40. (withdrawn) The fluorine-modified polyurethane resin of claim 30, wherein low molecular mass polyamine component (E) is an(cyclo)aliphatic and/or aromatic polyamine and/or amino alcohol.

41. (withdrawn) The fluorine-modified polyurethane resin of claim 30, wherein the low molecular mass polyamine component (E) latent is a curing agent based on an aldimine and/or a ketimine and/or an enamine.

42. (withdrawn) The fluorine-modified polyurethane resin of claim 30, wherein formulating component (F)(i) and (F)(ii) is a defoamer, a devolatilizer, lubricity and a flow-control additive, a dispersing additive, a substrate wetting additive, a water repellent, a rheology additive, a coalescence assistant, a matting agent, an adhesion promoter, an antifreeze agent, a antioxidant, a UV stabilizer, a bactericide, a fungicide, a further polymer, a filler, a pigment, or a nanoparticle, or a suitable combination thereof.

43. (withdrawn) The fluorine-modified polyurethane resin of claim 30, wherein the NCO/OH equivalent ratio of components (A1), (A2), (A3)(i), and (B)(i) in stage a) is set at a level of 0.5 to 10.0.

44. (withdrawn) The fluorine-modified polyurethane resin of claim 30, wherein the NCO/OH equivalent ratio of components (A4) and (B)(ii) in stage c₁) is set at 1.9 to 2.1 and the NCO/OH+NH equivalent ratio of the components in the preadduct from stage c₁) and (C)(ii) in stage c₂) is set at 0.95 to 1.05.

45. (withdrawn) The fluorine-modified polyurethane resin of claim 30, wherein the NCO/OH equivalent ratio of binder and curing agent in stage b) is set at a level of 1.0 to 2.0.

46. (withdrawn) The fluorine-modified polyurethane resin of claim 30, wherein reaction stages a), b), and c) are carried out in the presence of 0.01% to 1% by weight, based on components (A) and (B), of a catalyst which is customary for polyaddition reactions with polyisocyanates.

47. (withdrawn) The fluorine-modified polyurethane resin of claim 30, wherein in stage a) the solids content of fluorine-modified polyurethane prepolymer or polyol mixture, consisting of components (A1), (A2), (A3)(i), (B)(i), and (C)(i), is set at 25% to 100% by weight based on the total amount of the binder, consisting of components (A1), (A2), (A3)(i), (B)(i), optionally (C)(i), (F)(i), optionally (L)(i) and optionally (L)(iii).

48. (withdrawn) The fluorine-modified polyurethane resin of claim 47, wherein in stage a) the solids content of fluorine-modified polymethane prepolymer or polyol mixture is set at 50% to 75% by weight, based on the total amount of the binder.

49. (withdrawn) The fluorine-modified polyurethane resin of claim 30, wherein in stage b) the solids content of crosslinker component, consisting of components (B)(iii) and (B)(iii) or (A3)(ii) and/or (E), respectively, is set at 25% to 100% by weight, based on the total amount of curing agent (D), consisting of components (B)(iii) or (A3)(ii) and/or (E), (F)(ii) and, optionally, (L)(iii).

50. (withdrawn). The fluorine-modified polyurethane resin of claim 49, wherein in stage b) the solids content of crosslinker component is set at 50% to 75% by weight, based on the total amount of the curing agent (D).

51. (withdrawn) The fluorine-modified polyurethane resin of claim 30, wherein the polyurethane polymer, consisting of components (A), (B), (C), and (E), has an average molecular mass (number average) of 10,000 to 100,000 daltons.

52. (withdrawn) A process for preparing the fluorine-modified polyurethane resin of claim 30, wherein

a) a fluorine-modified polyurethane prepolymer or polyol mixture (binder) is prepared by

a₁) reacting components (A1), (A2), and (A3)(i) either with component (B)(i) optionally in the presence of a solvent component (L)(i) and optionally in the presence of a catalyst, some or all of the hydroxyl groups of components (A1), (A2), and (A3)(i) being reacted with the isocyanate groups of component (B)(i), or blending said components optionally in the presence of a solvent component (L)(i) and in the optional presence of a catalyst,

a₂) optionally reacting the fluorine-modified polyurethane prepolymer or the polyol mixture from stage a₁) with an optionally fluorine-modified functionalizing component (C)(i),

a₃) admixing the fluorine-modified polyurethane prepolymer or polyol mixture from stages a₁) or a₂) with a formulating component (F)(i), the formulating constituents being added individually or together before, during or after the reaction or blending of the individual components, and

b) a fluorine-modified polyurethane resin is prepared by reacting the fluorine-modified polyurethane prepolymer from stage a₃) in the case of a one-component application with atmospheric moisture, or reacting the fluorine-modified polyurethane prepolymer or polyol mixture from stage a₃) (binder) in the case of a two-component application with a crosslinker component (D) (curing agent), a formulating component (F)(ii), and, optionally, a solvent component (L)(iii), optionally in the presence of a catalyst, using as crosslinker component (D) in the case of the polyol mixture a polyisocyanate component (B)(iii) and in the case of the polyurethane prepolymer a polyisocyanate component (B)(iii) or a low molecular mass polyol component (A3)(ii) and/or a low molecular mass polyamine component (E), and adding the formulating constituents individually or together before, during or after the blending of the individual components.

53. (withdrawn) The process of claim 52, wherein the fluorine-modified macromonomer (A1) is prepared by

c₁) reacting a fluoro alcohol component (A4) with the polyisocyanate component (B)(ii) optionally in the presence of a solvent component (L)(ii) and optionally in the presence of a catalyst, the reaction conditions and the selectivities of components (A4) and (B)(ii) being chosen such that only one isocyanate group of component (B)(ii) reacts with component (A4), and subsequently

c₂) optionally reacting the preadduct from stage c₁) completely with the functionalizing component (C)(ii), the reaction conditions and the selectivity of component (C)(ii) being chosen such that only one reactive group of component (C)(ii) reacts with the free isocyanate group(s) of the preadduct.

54. (withdrawn) The process of claim 51, wherein reaction stages a₁) and a₂) are carried out at a temperature of from 40 to 120°C.

55. (withdrawn) The process of claim 54, wherein the process is performed at a temperature of 50 to 110°C.

56. (withdrawn) The process of claim 51, wherein reaction stages a₃) and b) are carried out at a temperature of from 10 to 60°C.

57. (withdrawn) The process of claim 56, wherein the process is carried out at a temperature of 20 to 50°C.

58. (withdrawn) The process of claim 51, wherein reaction stages c₁) and c₂) are carried out at a temperature of from -20 to 50°C.

59. (withdrawn) The process of claim 58, wherein the process is performed at a temperature of 0 to 30°C.

60. (currently amended) A method comprising providing a permanent oil- and water-repellent surface treatment or modification of a mineral substrate and nonmineral substrates by applying the fluorine-modified polyurethane resin of claim 30 to a mineral or nonmineral substrate on an amount sufficient to provide a permanent oil- and water- repellent surface thereon, wherein the fluorine-modified polyurethane resin is a prepared by a process comprising the steps of

a) preparing a fluorine-modified polyurethane prepolymer having free isocyanate groups or free amino and/or hydroxyl groups, or a fluorine-modified polyol mixture having free hydroxyl groups (binder), by

a₁) a fluorine-modified macromonomer (A1) having two or more groups selected from the group consisting of amino and hydroxyl that are reactive toward isocyanate groups and having a molecular mass of 500 to 2000 daltons, a higher

molecular mass polyol component (A2) having two or more hydroxyl groups that are reactive toward isocyanate groups and having a molecular mass of 500 to 6000 daltons, and, optionally, a low molecular mass polyol component (A3)(i) having two or more hydroxyl groups that are reactive toward isocyanate groups and having a molecular mass of 50 to 499 daltons

either

is reacted with a polyisocyanate component (B)(i), consisting of at least one diisocyanate, polyisocyanate, polyisocyanate derivative or polyisocyanate homolog having two or more (cyclo)aliphatic or aromatic isocyanate groups of same or different reactivity, optionally in the presence of a solvent component (L)(i) and optionally in the presence of a catalyst,

or

is blended in the presence of a solvent component (L)(i) and optionally in the presence of a catalyst,

a2) the fluorine-modified polyurethane prepolymer or polyol mixture from stage a1) is optionally reacted with an unmodified or fluorine-modified functionalizing component (C)(i) having one or more groups selected from the group consisting of amino and hydroxyl that are reactive toward isocyanate groups and/or one or more isocyanate groups that are reactive toward hydroxyl groups and having a molecular mass of 50 to 2500 daltons, selected from the group consisting of (cyclo)aliphatic polyols, aromatic polyols, polyamines, polyamino alcohols and reactive polyhedral oligomeric polysilsesquioxanes (POSS) of the general formula $(RSiO_{1.5})_n$ wherein n is 4, 6, 8, 10 or 12 and wherein R is any organic residue having 1 to 100 C atoms and

from 0 to 50 atoms selected from the group consisting of N, O, F, Si and S or a combination thereof, and a molar mass of 250 to 25,000 daltons.

a₃) the fluorine-modified polyurethane prepolymer or polyol mixture from stages a₁) or a₂) is admixed with a formulating component (F)(i), and finally

b) by preparing a fluorine-modified polyurethane resin having a polymer-bonded fluorine content of 1% to 4% by weight in the system as a whole by reacting the fluorine-modified polyurethane prepolymer from stage a₃) in the case of a one-component application with atmospheric moisture, or reacting the fluorine-modified polyurethane prepolymer or polyol mixture from stage a₃) (binder) in the case of a two-component application with a crosslinker component (D) (curing agent), with a formulating component (F)(ii) optionally in the presence of a solvent component (L)(ii) and also of a catalyst, using as crosslinker component (D) in the case of the polyol mixture from stage a₃) a polyisocyanate component (B)(iii) consisting of at least one diisocyanate, polyisocyanate, polyisocyanate derivative or polyisocyanate homolog having two or more (cyclo)aliphatic or aromatic isocyanate groups of same or different reactivity and in the case of the polyurethane prepolymer a polyisocyanate component (B)(iii) or a low molecular mass polyol component (A3)(ii) having two or more hydroxyl groups that are reactive toward isocyanate groups and having a molecular mass of 50 to 499 daltons and/or a low molecular mass polyamine component (E) having two or more (cyclo)aliphatic or aromatic amino groups that are reactive toward isocyanate groups and having a molecular mass of 50 to 500 daltons.

61. (currently amended) The method of claim 60, wherein the mineral substrate is an and nonmineral substrates are inorganic surface surfaces.

62. (currently amended) The method of claim 61, wherein the inorganic surface is ~~surfaces are~~ selected from the group consisting of porous, absorbent, rough and polished construction material, an enamel, a filler and a pigment, a glass, a ceramic, a metal and a metal alloy.

63. (currently amended) The method of claim 60, wherein the mineral ~~and nonmineral substrates are~~ substrate further comprises an organic surface surfaces.

64. (currently amended) The method of claim 61 wherein the organic surface surfaces are selected from the group consisting of wood, a woodbase material, a wood veneer, a glass fiber-reinforced plastic (GRP), a plastic, ~~leather, a~~ a natural fiber, a polar organic polymer, or a composite material.

65. (previously presented) The method of claim 60, wherein the coating is an

antigraffiti/antisoiling coating; a easy to clean coating, a coating for a seal; a prefabricated concrete component, an adhesive, a sealant, a soundproofing for a wall, a corrosion control, a render or a decorative plaster, an external insulation and finishing system (EIFS) and external insulation system (EIS)

66. (previously presented) The method of claim 65, wherein the coating is a balcony coating, a roof(tile) coating, a baking varnished, a paint, a varnish, a masonry paint, a floor coating, a light-, medium- and heavy-duty industrial floors, a carpark surfacings or a sports floor.

67. (currently amended) The method of claim 60, wherein the coating is applied as an automotive coating, a coil coating, a baking varnish, a glass façade, and glass surface,

a ceramic, a ~~leather dressing~~, a surface-modified filler, a pigment a paper coating, a rotor of wind turbines, marine paints.

68. (currently amended) The method of claim 60, wherein the method is performed in the construction or industrial sector for the integral water/oil repellency treatment of concrete.

69. (currently amended) The method of claim 60, wherein ~~the, wherein it~~ comprises concrete for prefabricated concrete components, concrete moldings, cast-in-place concrete, shotcrete, and ready-mix concrete.

70. (withdrawn) The fluorine-modified polyurethane resin of claim 31, wherein as fluorine-modified macromonomer (A1) use is made of reaction products and/or macromonomers, with a monomodal molar mass distribution, of monofunctional perfluoroalkyl alcohols, isophorone diisocyanate or toluene diisocyanate, and diethanolamine.